SCIENCE FOR GLASS PRODUCTION

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MELTING REFRACTORY BOROSILICATE GLASS IN ELECTRIC FURNACES

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The advantages of melting refractory borosilicate glasses in electric furnaces as compared to gas furnaces are described. The processes that occur in liquid glass melted in deep electric furnaces and technologies producing liquid glass of high quality are considered.

Refractory borosilicate glasses of grades SL40-1 (Russia), Pyrex (USA), Simax (Czech Republic), B40 (France), GGL4-31 (Germany), V712 (Hungary), and SL41-1 (Poland) with up to 20 wt.% B_2O_3 are widely used in the electrovacuum, light and chemical industries for production of thin-wall shells of electrovacuum devices, light sources, and chemical glassware and pipes.

Melting of these glasses is complicated. The main obstacle consists in the evaporation of boron compounds from the batch and from the surface of the liquid glass in the form of alkali borates. This causes the formation of a surface crust in the melting part of the furnace and in the feeder, and the apperance of such defects as stones, stria, thread or tear-shaped flaws.

In most cases, refractory glass is melted in cross- or end-fired gas regenerative furnaces. They are low-efficiency, consume much fuel, occupy a large area in the shops, require many refractories for erection and repair and, what is most important, produce glass with the mentioned defects [1].

The practical experience of the leading firms, i.e., Corning Glass (USA) and Covalier (Czech Republic), shows that the electric method is better for melting borosilicate glass.

The surface evaporation of boron compounds in electric furnaces is reduced to a minimum; stones, stria and threads are virtually absent in the melted glass and the chemical composition and viscosity of the latter are more uniform.

Electric furnaces are very efficient, occupy a small area in the shop, and are ecologically clean.

Glass melting in electric furnaces has features that distinguish it from the process in gas furnaces. In the former, melting is conducted in the vertical direction. At 1560 – 1580°C, the viscosity of the liquid glass on the surface attains $10^{1.3}$ – $10^{1.5}$ Pa · sec. Therefore, fine bubbles evaporate freely from the liquid glass. The latter is well homogenized. The surface of the liquid glass in the second part of the melting furnace is commonly free of foam. The cristobalite crust on the surface of the front part is easily removed by an increase in the temperature, creation of neutral pressure, or under the weakly reducing action of the gas medium at the level of the glass surface [2]. When changing the kind of product, a decrease or increase of the yield virtually does not affect the quality of the liquid glass.

Melting in electric furnaces occurs in the vertical direction. Several temperature zones with different melting rates form in the volume of the glass in the process. In the center, the melting rate is always higher than near the walls. This depends on self-regulation of the furnace and is caused by the high temperature of the liquid glass in the given volume. Electrical current always tends to pass through the zone with a higher temperature and much lower viscosity of the liquid glass.

Electric furnaces are very sensitive to a variation in the hourly output. With an increase or decrease in the latter, the thickness of the layers of the batch mixture and scrap that covers the entire surface of the melting part changes. Let us conside two variants.

The hourly production of the furnace increases. In this case the thickness of the layer increases. As a result, the upper boundary layer of the liquid glass under the batch will cool and the viscosity will increase. The viscosity of borosilicate glass can fluctuate from $10^{3.5}$ to $10^{4.8}$ Pa · sec, which increases the electric resistivity of the liquid glass and shifts the electrical and the temperature fields into the depth of the furnace. The residence time of the liquid glass in the maximum

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temperature zone decreases. The liquid mixture does not have enough time for homogenization and its physical inhomogeneity fluctuates within a wide range. In a nonuniform mixture, the viscosity over the cross section of the drop is unstable, which results in nonuniform distribution of the liquid glass in the molded parts in the production of thin-wall vessels or pipes. This decreases the yield of high-quality products.

The hourly production of the furnace decreases. In this case the electric and the thermal fields shift upwards and the batch and scrap layer virtually does not form or has an inconsiderable thickness. A thin (20 – 30 mm) viscous ($30^{3.9} - 10^{5.25}$ Pa · sec) crust can appear and hamper the removal of the gases, which results in the formation of seeds and fine blisters; gases can also partially dissolve in the liquid glass [3].

The mixed layer of batch with scrap should have a stable thickness on the surface of the liquid glass. Its fluctuation to any side is inadmissible because it leads to a change in the position of the hot spot. Liquid glass of the requisite quality is obtained if it is as close as possible to the surface layer.

This can be attained by increasing markedly the electrical conductivity of the liquid glass under the mixed layer by

introducing chlorine or fluorine compounds into the batch;

eliminating compounds containing water of hydration from the batch;

using dry fine-grain scrap;

preparing the batch from sand with grains 0.1 – 03 mm in size.

The chlorine compounds contained in the batch decrease the viscosity of the liquid glass and promote passage of the electric current between the electrodes by the upper path.

The size of scrap pieces is important for melting refractory high-viscosity glass in an electric furnace. Large-piece scrap does not have enough time to react with the batch because the rate of silicate and glass formation in the melting batch is higher than that of the interaction between the batch and the scrap. The unreacted scrap softens and forms a crust on the surface through which gases cannot penetrate and be removed. A similar crust appears on the surface when the scrap is milled to a powder state. The gases concentrate under the crust forming a layer and creating high pressure. As a result, the liquid glass cannot be refined fully. Some of the gas dissolves in the liquid glass in the amount of 0.75 l per 100 g of glass. It contains 2.4 – 2.7 vol.% CO_2, 18 – 29 vol.% $CO + N_2$, 14 – 17 vol.% H_2, and 61 – 63 vol.% H_2O. The unrefined liquid glass passes to the shaping part of the furnace, as a result of which the finished products contain seeds and blisters. When the physical equilibrium of the liquid gases in the atmosphere of the melting part and the feeder is disturbed, the finished products can also contain seeds and blisters.

The optimum size of the pieces should be 20 – 30 mm. The scrap should be absolutely dry and magnetically separated.

The water of hydration contained in some components of the batch is removed at a very high temperature, cooling the boundary layer of the liquid glass and promoting the formation of a surface crust.

Quartz sand with grains less than 1 mm and over 0.3 mm in size slows the melting process.

In order to prevent the formation of numerous seeds inside the finished products, the batch should be prepared from raw materials that can be degassed before the appearance of a vitreous phase. In order to prevent the formation of a crust on the surface of the liquid glass in the melting part of the furnace, the scrap should be mixed with the batch. This can be done in three ways, namely,

mixing them right in the mixer;

mixing by layers when loading the batch into the bucket;

mixing by a special device placed directly on the batch loader.

In all cases, the interaction between the batch and the scrap in melting occurs more rapidly, which creates the prerequisites for sustaining the mixed layer in a loose state. This layer lets through virtually all gases formed in refining of liquid glass, and the oxides evaporating from the melt are condensed in it to a fuller degree.

When melting refractory high-viscosity glasses in an electric furnace, the maximum temperature in the hot spot should be sustained at a level of 1560 – 1580°C. Our practice shows that this temperature range is optimum. It provides for a uniform melting rate in specific zones of the furnace and stabilizes the hourly output in shaping the products. Even slight elevation of the temperature above the indicated limit markedly accelerates corrosion of the refractories and increases their electrical conductivity. The leakage currents increase too. The refractories are additionally heated and their corrosion intensifies. This decreases the service life of the furnace and increases the specific consumption of electric power.

In order to form ascending convective currents that impede inflow of poorly conditioned liquid glass into the discharge flow, the areas of the vertical sections from the top part to the bottom of the melting part of furnaces for melting refractory glass should decrease stepwise in order to eliminate stagnation zones. Artificial barriers direct the unrefined liquid glass into the zone of high temperatures and thus create prerequisites for increasing its residence time there, which has a favorable effect on stabilization of the physicochemical properties of the glass.

It is expedient to position vertical molybdenum electrodes in the bottom of the melting part over its longitudinal axis; these will also form ascending flows. In combination with the artificial barriers, they create conditions that hamper penetration of poorly conditioned liquid glass into the shaping part of the furnace.

In order to prolong the service life of the beams that cut the flow, they should be coated from the inside and on the end face by molybdenum sheets. Our experience proves the expediency of this design.

Two rows of molybdenum electrodes should be mounted in the melting part of electric furnaces for melting refractory

glass; the electrodes of the lower row should have the shape of plates and those of the upper row should have the shape of rods. This has been proved by the experience of the Gomel glass plant in melting Pyrex glass and that of the Covalier firm (Czech Republic) in melting Simax glass. A multirow system of electrodes makes it possible to obtain the requisite temperature curve over the depth of the melting pool with the hot spot positioned closer to the surface.

In melting refractory glass in an electric furnace, one special feature has to be taken into account. As a rule, the liquid glass arriving from the melting part of the furnace in the shaping part has a layered structure. Due to the difference in the surface tension and the weak diffusion between the layers, the viscosity of the liquid glass in the feeder and in the bowl cannot level out and such liquid glass arrives for shaping. As a result, the shells have different thicknesses and pipes are characterized by ellipticity and taper. In order to level the viscosity characteristics in moving to the shaping zone, the shaping part should have a large volume and the path of movement should be long.

Since the furnace is commonly designed for products with a mean statistical drop mass, the volume of the shaping part and the length of the feeders can be insufficient, which will worsen the quality of the products.

In order to prevent this situation and improve the homogeneity of the liquid glass, the vertical channel of the shaping part should be equipped with special homogenizers or stepover devices and the liquid glass itself should be heated by plate or rod electrodes.

The surfaces of the shaping part of the furnace and the feeder should be coated by plates made of electrofused refractories or nontransparent quartz glass. The roof space of the feeder should be heated by molybdenum disilicide heaters and the batch should be heated by molybdenum electrodes positioned in the enclosing walls.

The cristobalite crust formed on the surface of the liquid glass in the bowl should be removed through an escape beam directly from the bowl or just before it.

The temperature of the flow passing into the shaping part should be high and should decrease slowly with the distance from the bowl.

Special attention should be paid to spreading of the liquid glass in a ball when shaping thin-walled large articles. This is directly connected with the viscosity of the liquid glass in the surface and deep zones of the drop and primarily depends on the chemical and thermal homogeneity. We established that the thermal homogeneity is predominantly affected by the total content of iron oxides in the borosilicate liquid glass and primarily by iron in the Fe(II) form. Bivalent iron has a deep absorption band in the near IR region of the spectrum (900 – 1100 nm).

When shaping large products, liquid glass containing iron in the Fe(II) form hardens much more rapidly and spreads more slowly in the external layers because it intensely emits heat into the environment when cooled. The viscosity of the external layers increases markedly, whereas that of the internal layers remains low. This causes thickening of the wall in the neck when shaping gas-discharge bulbs and thinning of the wall in their parabolic part, which decreases the strength of the bulbs. In addition to reducing the total content of iron (Fe(II) + Fe(III)) special techniques should be used for sustaining the Fe(II) content at a level not exceeding 20 – 25% of the total iron content in the liquid glass.

The use of the considered design and methods in melting refractory borosilicate glass in an electric furnace gives high-quality liquid glass and increases the service life of the furnace.

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